

Remarks:

Claims 1-6, 9-11, 13-14, 16, 18, and 20-28 remain pending in the Subject Application. Claims 7, 8, 12, 15, 17, 19, and 29-98 were cancelled in a previous response. Claims 6, 14, 23-24, and 27-28 are withdrawn from consideration. Claims 1-5, 9-11, 13, 16, 18, 20-22, and 25-26 stand rejected. Claims 3-4 and 9 are amended herein to correct antecedent basis and have no effect on patentability. Applicant expresses his appreciation for the withdrawal of all previous objections and rejections in view of Applicant's amendments and arguments.

Claim Rejections 35 U.S.C. § 103(a) – Szummer in view of Ono

On page 3 of the Office Action, the Examiner rejects claims 1-5, 9-11, 16, 18, 20-22 and 25-26 under 35 U.S.C. § 103(a) as being unpatentable over Szummer et al., *Hydrogen surface effects in ferritic stainless steels*, J. Alloys Compounds 293-295 (1999) pp. 356-360 ("Szummer") in view of Japanese patent publication number JP 10-280103 to Ono ("Ono").

Claims 1, 10 and 11

In regards to claims 1, 10 and 11, the Examiner alleges that Szummer discloses a method for preparing ferritic stainless steels containing 16 weight percent, 17 weight percent and 19.3 weight percent chromium that comprises electropolishing the stainless steel (page 356, column 2). The Examiner concedes that Szummer does not disclose a method of preparing stainless steels that comprise at least 0.2 weight percent aluminum and a total weight of rare earth metals from 0.02 to 1.0 weight percent.

Applicant respectfully submits that the Examiner has mischaracterized Szummer. Szummer mentions, almost in passing, that preparing the samples discussed in Szummer for microscopic analyses involved a step of electropolishing. It is well known in the art of metallographic examination that electropolishing is used to prepare metallic samples for microscopic examination. In the ASM Materials Engineering Dictionary, electropolishing is defined as:

A technique commonly used to prepare metallographic specimens, in which a high polish is produced making the specimen the *anode* in an *electrolytic cell*, where preferential dissolution at high points smooths the surface. Also referred to as *electrolytic polishing*.¹

That same text defines electrolytic polishing as:

An electrochemical polishing process in which the metal to be polished is made the *anode* in a electrolytic cell where preferential dissolution at high points in the surface topography produces a specularly reflective surface Also referred to as *electropolishing*.²

(Emphases in original).

There are at least two reasons metallographers use electropolishing to prepare specimens of metallic samples for optical and electron microscopic analyses. First, an electropolished surface is highly smooth and reflective, which facilitates detection of second phases in the microstructure of the metal or metal alloy. Second, for examination at higher magnifications, such as when using transmission electron microscopy (TEM), electropolishing is used to thin metal foil specimens to a thickness whereby electrons from the microscope can penetrate the thinned metal foil to image (and chemically analyze) the thin foil specimen.

Electropolishing of stainless steels for metallographic examination is described in the "Metallographic Practices for Wrought Stainless Steels" chapter of the ASM Specialty Handbook of Stainless Steels³ (attached). Page 440 of the reference states:

Stainless steels, particularly austenitic grades are often polished electrolytically. In most cases, electropolishing is performed after grinding to a 600-grit silicon carbide finish. Table 2 lists recommended procedures. Electropolishing produces high-quality, deformation free surfaces;

¹ ASM Materials Engineering Dictionary, Fifth Printing", ed. by J. R. Davis, ASM International (January 2006) p. 141.

² *Id* at 139.

³ ASM Specialty Handbook of Stainless Steels, ed. by J. R. Davis, ASM International, Materials Park, OH (December 1994) pp. 440-444.

Table 2 of the reference lists six different electropolishing procedures for metallographic sample preparation of stainless steels for microscopic analyses. Further, in the middle column of page 443 of the same reference, Table 4 lists seven electropolishing procedures for preparing thin-foil stainless steel specimens for TEM.

Szummer uses electropolishing to prepare ferritic stainless steel specimens for studying the "surface microstructure of ferritic chromium stainless steels subjected to hydrogen charging". (Abstract – emphases added.) Szummer states that:

After cutting, the specimens were first mechanically polished and then electropolished TEM specimens were prepared by preliminary electrolytic thinning without perforation, then cathodically charged and thinned from one side by electrochemical polishing until perforation. The H-charged surface was left unaffected by the preparation procedure so that the H-induced microstructural changes in the sample could be examined ... using optical, scanning and transmission electron microscopes

(Page 356, column 2; emphases added). Szummer does not use electropolishing as a step in a "method for making a ferritic stainless steel article having an oxidation resistant surface", as recited in the preambles of claims 1, 10 and 11 of the Subject Application (emphases added).

Clearly, Szummer does not disclose or even suggest that electropolishing could be used as a "method for making a ferritic stainless steel article having an oxidation resistant surface". Instead, the experimental work in Szummer studied "H-induced microstructural changes" in ferritic steel. Szummer introduced hydrogen into the metal samples by cathodic charging, *i.e.*, the metal sample was made the cathode in the charging electrolyte. The TEM specimens were (then) thinned by electrochemical polishing until perforation. The H-charged surface was left unaffected by the preparation procedure. In other words, in Szummer: (1) the ferritic stainless steel TEM samples were electrolytically thinned while anodically polarized in an unspecified electrolyte; (2) one surface was then charged with hydrogen atoms while cathodically polarized in sulfuric acid electrolyte; and (3) the surface that was not charged was

thinned by electrochemical polishing (anodically polarized) until perforation in an unspecified electrolyte, while leaving the cathodically charged surface unaffected.

On page 7 of the Office Action, in regards to claim 25, the Examiner alleges that Szummer achieves thinning (impliedly) by electropolishing the ferritic stainless steel in a 1N H₂SO₄ (sulfuric acid) solution and passing a 0.1 A/cm² current to perform the thinning or weight removal (page 356, column 2). Applicant respectfully submits that the Examiner has mischaracterized the sample preparation technique used by Szummer. Szummer introduced hydrogen to the ferritic steel by "cathodic charging" in sulfuric acid solution, and did not use the sulfuric acid solution for thinning. During cathodic charging with hydrogen, the ferritic steel was made the cathode and a "platinum anode" was used. Selenium dioxide (SeO₂) also was added as a "hydrogen recombination poison" to prevent the hydrogen atoms that are formed at the ferritic stainless steel / sulfuric acid electrolyte interface from recombining to form molecular hydrogen instead of diffusing into and reacting with the ferritic stainless steel.

Szummer lacks any teaching, suggestion, or motivation to use electropolishing on a ferritic stainless steel alloy comprising at least 0.2 weight percent aluminum, at least one rare earth metal and 16 to less than 30 weight percent chromium, wherein the total weight of rare earth metals is from 0.02 to 1.0 weight percent to produce an oxidation resistant surface as recited in claims 1, 10 and 11 of the Subject Application.

As discussed hereinabove, electropolishing is accomplished with the workpiece configured as the anode. The metallographic art of electropolishing stainless steels for metallographic microscopic examination is so well known in the art that Szummer does not even disclose the conditions that were used for electropolishing in the experiments of Szummer. However, there is absolutely no reason why a person having ordinary skill in the art would look to Szummer to develop a "method for making a ferritic stainless steel article having an oxidation resistant surface". While Szummer merely mentions electropolishing ferritic stainless steels for metallographic analysis, there is no teaching or suggestion that electropolishing would be an effective means to prepare an oxidation resistant surface on ferritic stainless steel.

On page 4 of the Office Action, the Examiner maintains that, in the same field of endeavor (as Szummer), Ono discloses adding 0 to 1 weight percent aluminum and 0 to 0.2 weight percent of rare earth metals to a ferritic stainless steel alloy having the same level of chromium as Szummer et al. to improve oxidation (corrosion) resistance. Ono at paragraphs [0017] and [0019]. The Examiner maintains that, therefore, it would have been obvious to one of ordinary skill in the art at the time the invention was made to have added 0 to 1 weight percent aluminum and 0 to 0.2 weight percent rare earth metals, as disclosed by Ono, to the ferritic stainless steel disclosed in Szummer, in order to improve oxidation (corrosion) resistance, as disclosed by Ono.

Applicant disagrees. Applicant maintains that while Ono may disclose a stainless steel alloy comprising ranges of chromium, aluminum and rare earth metals that overlap with compositions recited in independent claims 1, 10 and 11 of the Subject Application, the composition of the alloy is only relevant in that it is likely that the steel of Ono will form an oxidation resistant surface by following the methods recited in claims 1, 10 and 11 of the Subject Application. The English language abstract of Ono refers to a steel that forms a "good" oxidized coating having "good" electric conductivity at 1000°C. Applying the inventive methods recited in claims 1, 10 and 11 of the Subject Application to the steel disclosed by Ono, including electropolishing the steel to form an oxidation resistant surface, is likely to increase the high temperature oxidation resistance of the steel disclosed by Ono by several orders of magnitude (see paragraph [0056] of the Subject Application), *i.e.*, an oxidation resistant surface will likely be formed on the steel of Ono as recited in claims 1, 10 and 11 of the Subject Application. The methods recited in claims 1, 10 and 11 of the Subject Application are directed to forming an oxidation resistant surface on ferritic stainless steels having compositions recited in claims 1, 10 and 11.

Szummer merely discloses that electropolishing can be used for metallographic sample preparation of ferritic stainless steels for microscopic analysis. Applicant, however, believes that it has never been taught or suggested that electropolishing may be used to form a surface on a ferritic stainless steel that is resistant to oxidation at high temperatures, such as the temperatures of 750°C-850°C used in the experiments

described in the Subject Application. Regarding prior applications of electropolishing of stainless steels for purposes other than metallographic sample preparation, Applicant notes:

It is known to electrochemically modify the surfaces of certain austenitic stainless steels. For example, it is known to electropolish certain austenitic stainless steels used in medical and pharmaceutical applications to provide surfaces that are clean and generally free of crevices. However, electropolishing or otherwise electrochemically modifying the surfaces of ferritic stainless steels is not generally applied, and it has not heretofore been considered useful to electropolish stainless steels to improve their high temperature oxidation resistance properties.

(As-filed Subject Application paragraph [0050]; emphases added).

Simply because other stainless steels comprise compositions that fall with the ranges recited in claims 1, 10 and 11 would not have rendered the methods recited in claims 1, 10 and 11 obvious. Examination of the Subject Application, e.g., Figure 9, demonstrates that the method does not work as well with stainless steels that do not have the compositions recited in claims 1, 10 and 11. There is absolutely no teaching, suggestion, or motivation in the cited art to use electrolytic polishing to improve high temperature oxidation resistance of ferritic steels having the composition recited in claims 1, 10 and 11 of the Subject Application. At least for the above reason, Applicant maintains that the Examiner has not established a *prima facie* case of obviousness and the rejections over Szummer in view of Ono should be withdrawn.

In light of the Supreme Court's decision in *KSR International Co. v. Teleflex Inc.*, 82 USPQ2d 1385 (S. Ct., 2007) ("KSR"), the MPEP includes guidelines for determining obviousness under § 103 ("Guidelines"). The Guidelines reiterate that the framework for the objective analysis for determining obviousness lies in *Graham v. John Deer Co.*, and that obviousness is a question of law based on the following three underlying factual inquiries:

- (1) Determining the scope and content of the prior art;
- (2) Ascertaining the differences between the claimed invention and the prior art; and
- (3) Resolving the level of ordinary skill in the pertinent art.

See MPEP 2141(II).

The Guidelines further articulate the following concerning the Examiner's role in assessing obviousness:

When making an obviousness rejection, Office personnel must therefore ensure that the written record includes findings of fact concerning the state of the art and the teachings of the references applied.

Once findings of fact are articulated, Office personnel must provide an explanation to support an obviousness rejection under 35 U.S.C. 103. 35 U.S.C. 132 requires that the applicant be notified of the reasons for the rejection of the claim so that he or she can decide how best to proceed. *Id.* (emphasis added).

The key to supporting any rejection under 35 U.S.C. 103 is the clear articulation of the reason(s) why the claimed invention would have been obvious. The Supreme Court in *KSR* noted that the analysis supporting a rejection under 35 U.S.C. 103 should be made explicit.

See MPEP 2141(III) (emphases added). The Guidelines also state as follows:

Prior art is not limited just to the references being applied, but includes the understanding of one of ordinary skill in the art. The prior art reference (or references combined) need not teach or suggest all claim limitations; however, Office personnel must explain why the difference(s) between the prior art and the claimed invention would have been obvious to one of ordinary skill in the art.... The gap between the prior art and the claimed invention may not be 'so great as to render the [claim] nonobvious to one reasonably skilled in the art.'

MPEP 2141(III) (emphasis added).

Of the rejected claims, claims 1, 10 and 11 are independent. In the case at hand, and as discussed below, the gap between the teachings in the cited references and the subject matter recited in independent claims 1, 10 and 11 is "so great as to render the [claims] nonobvious to one reasonably skilled in the art."

Claims 1, 10 and 11 require "electropolishing at least one surface of the ferritic stainless steel." The Examiner has provided no explicit rationale in the Office Action as to why one of ordinary skill in the art, when considering Szummer in view of Ono, would be motivated to electropolish a ferritic stainless steel for any other reason than

metallographic sample preparation, much less than for making an oxidation resistant surface on the ferritic stainless steel. Thus, the gap between the teachings in the cited reference and the subject matter recited in independent claims 1, 10 and 11 is "so great as to render the [claims] nonobvious to one reasonably skilled in the art". Accordingly, Applicant respectfully requests withdrawal of the rejection of claims 1, 10 and 11 over Szummer in view of Ono.

As discussed above, the Guidelines included in the MPEP discussing how examiners are to assess obviousness require that an Office Action include the examiner's findings pursuant to the *Graham v. John Deere* factors, as well as a "clear articulation of the reason(s) why the claimed invention would have been obvious." In *KSR, supra*, the Supreme Court ruled that to support an obviousness rejection, an analysis of obviousness should be made wherein the patent examiner assesses "whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue." The Court further stated that "[t]o facilitate review, this analysis should be made explicit." Also, in response to the *KSR* decision, prior to the PTO's publication of the Guidelines, the Deputy Commissioner for Patent Operations stated in a May 3, 2007 memo to the Patent Office's Technology Center Directors that "in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed."

Therefore, the case law and the MPEP hold that an examiner cannot arbitrarily combine teachings of prior art references so as to achieve a claimed invention. Instead, there must be a rational basis for an examiner to combine reference teachings in a § 103(a) rejection, and the examiner must identify that basis in an Office Action. Thus, as the case law and the MPEP amply support, absent there being a stated rational basis for combining reference teachings in the manner an examiner sets forth in an obviousness rejection, the examiner has not established a *prima facie* case that the claimed invention would have been obvious. See also MPEP 2142. ("The examiner bears the initial burden of factually supporting any *prima facie* conclusion of obviousness.... However, impermissible hindsight must be avoided and the legal

conclusion must be reached on the basis of the facts gleaned from the prior art.") ("The initial burden is on the examiner to provide some suggestion of the desirability of doing what the inventor has done."); MPEP 706.02(j) ("After indicating that the rejection is under 35 U.S.C. 103, the examiner should set forth in the Office action ... (D) an explanation why one of ordinary skill in the art at the time the invention was made would have been motivated to make the proposed modification."); *also see Ex parte Clapp*, 227 USPQ 872, 973 (BPAI 1985) ("To support the conclusion ... the examiner must present a convincing line of reasoning as to why the artisan would have found the claimed invention to have been obvious in light of the teachings of the references").

In the case at hand, the Examiner has not established a *prima facie* case of obviousness for at least the reason that he has not identified a rational basis why one of ordinary skill in the art at the time the invention was made would have electropolished or otherwise electrochemically modified the steel of Ono (other than for metallographic sample preparation). On page 4 of the Office Action, the Examiner alleges that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have added 0 to 1 weight percent aluminum and 0.0.2 weight percent rare earth metals, as disclosed by Ono, to the ferritic stainless steel of Szummer in order to improve oxidation (corrosion) resistance, as described by Ono. However, claims 1, 10 and 11 of the Subject Application recite methods of improving the oxidation resistance of stainless steels that have similar compositions to that of Ono's, and do not merely claim a composition of matter. Therefore, the basis for obviousness asserted by the Examiner in the Office Action is not pertinent to the method claims pending in the Subject Application.

There is no rational basis set out in the Office Action as to why it would have been obvious to electropolish a ferritic stainless steel of any composition to produce an oxidation resistant surface, as recited in claims 1, 10 and 11 of the Subject Application. Szummer makes mention of using the known metallographic sample preparation technique of electropolishing for preparing samples for TEM. However, there is no suggestion or inference in Szummer that one could use electropolishing for anything other than conventional sample preparation for microscopic analysis. The Examiner

does not provide any basis as to why the metallographic technique used to prepare samples for microscopic analysis should or could be combined with a ferritic steel of Ono to provide an oxidation resistant surface on the ferritic steel of Ono. At least for this reason, the Examiner has not established a *prima facie* case of obviousness, and the rejections to the claims should be withdrawn.

The only possible apparent reason given in the Office Action for combining Szummer and Ono is that they are "in the same field of endeavor" as that of the Subject Application. Applicant disagrees. The field of endeavor of Szummer is to study hydrogen embrittlement of ferritic stainless steels. This field of endeavor is not even reasonably pertinent to that of the Subject Application, which is to develop a method to make a surface that is resistant to high temperature oxidation. A person looking at the effects of an oxygenated environment (an oxidizing environment) on a ferritic steel at high temperatures, would not look to a publication that examines the effects of a hydrogenated environment (typically a reducing environment) on a ferritic steel. For this additional reason, the Examiner has not established a *prima facie* case of obviousness, and the rejections to the claims should be withdrawn.

The Examiner admits that neither Szummer nor Ono specify the hematite structure that the Applicant discovered is formed when an electropolished surface comprising the composition recited in the claims is exposed to high temperatures.⁴ The Examiner alleges, however, that Szummer in view of Ono discloses the same or substantially the same composition and the same process (electropolishing). The Examiner maintains, therefore, that it would be expected that Szummer in view of Ono would have the hematite structure and the hematite lattice parameters as claimed in the Subject Application.

⁴ The relevant recitation in claim 1 is "so that, when subjected to an oxidizing atmosphere at high temperature, the electropolished surface develops an electrically conductive, aluminum-rich, oxidation resistant oxide scale comprising chromium and iron and having a hematite structure differing from Fe_2O_3 , α - Cr_2O_3 , and α - Al_2O_3 "; in claim 2 is "wherein lattice parameters differ from a_0 and c_0 of Fe_2O_3 , α - Cr_2O_3 , and α - Al_2O_3 "; and in claims 5 and 10 are "wherein the oxide scale is characterized by lattice parameters a_0 in the range of 4.95 to 5.04 Å and c_0 in the range of 13.58 to 13.75 Å".

As set forth in MPEP 2141.01(a), however, an obviousness rejection cannot be based on a theory of inherency. Instead, in order to rely on some allegedly inherent feature of the prior art when fashioning an obviousness rejection, the allegedly inherent feature must have been known at the time that the claimed invention was made.

Obviousness cannot be predicated on what is not known at the time an invention is made, even if the inherency of a certain feature is later established. *In re Rijckaert*, 9 F.2d 1531, 28 USPQ2d 1955 (Fed. Cir. 1993).

(Cited in MPEP 2141.01(a)).

The Office Action provides no evidence that the hematite structure and oxide surface lattice parameter features recited in the claims were known to be present when the claimed invention was made. The Examiner admits that these features are not specified in Szummer and Ono. Moreover, since electropolishing was primarily used for metallographic sample preparation for microscopy, it is unlikely that any person of ordinary skill in the art would have had any reason to measure the lattice parameters of an oxide scale on a electropolished ferritic steel after exposing the electropolished surface to a high-temperature oxidizing atmosphere. Therefore, the obviousness rejections based on inherency in the Office Action are improper. At least for this reason, the rejections over Szummer in view of Ono should be withdrawn.

Based on any or all of the arguments presented hereinabove, it is evident that the methods recited in independent claims 1, 10 and 11 would not have been obvious over Szummer in view of Ono. Applicant requests that the § 103(a) rejections of claims 1, 10 and 11 over Szummer in view of Ono be withdrawn.

Because independent claims 1, 10 and 11 would not have been obvious over Szummer in view of Ono, it follows that any claims that directly or indirectly depend from claims 1, 10 and 11 also would not have been obvious over the combination of Szummer and Ono. Therefore, Applicant requests withdrawal of the rejections based on Szummer and Ono as applied to claims 2-4 and 9, which ultimately depend from claim 1; and claims 13, 16, 18, 20-22 and 25-26, which ultimately depend from claim 11.

Claim Rejections 35 U.S.C. § 103(a) – Szummer in view of Linden

On page 8 of the Office Action, the Examiner rejects claims 1-5, 9-11, 13, 18, 21 and 25-26 under 35 U.S.C. § 103(a) as having been obvious over Szummer in view of international patent application publication WO 99/10554 to Linden et al. ("Linden").

The Examiner alleges that Szummer discloses a method of preparing ferritic stainless steels as described in the rejection over Szummer in view of Ono, but concedes that Szummer does not specify that the ferritic stainless steels comprise at least 0.2 weight percent aluminum and a total weight of rare earth metals from 0.02 to 1.0 weight percent. The Examiner maintains that Linden discloses ferritic stainless steels comprising 15 to 25 weight percent chromium, 3 to 7 weight percent aluminum (added to form a protective oxide layer), and 0 to 0.5 weight percent of cerium, lanthanum, yttrium, and hafnium (added to improve adhesion of the oxide layer). The Examiner holds that it therefore it would have been obvious to one of ordinary skill in the art at the time the invention was made to add 3 to 7 weight percent aluminum and 0 to 0.5 weight percent cerium, lanthanum, yttrium, and hafnium, as disclosed by Linden, to the ferritic stainless steels containing 16 weight percent, 17 weight percent and 19.3 weight percent chromium disclosed in Szummer, in order to form a protective oxide layer and improve adhesion of the oxide layer, as disclosed by Linden.

Applicant has established the deficiencies of Szummer as a primary reference in the above-discussed § 103(a) rejection of the claims of the Subject Application. For example, Szummer neither teaches nor suggests, and one having ordinary skill in the art would not have otherwise believed, that electropolishing a ferritic stainless steel would provide the features recited in claims 1, 10 and 11 of the Subject Application. No rational basis was provided for combining Szummer with Ono, and it was shown that an obviousness rejection could not be based on inherency when an inherent property was not known at the time the invention was made.

Applicant asserts the same arguments as bases for the withdrawal of the Examiner's § 103(a) rejections based on Szummer in view of Linden. Linden merely discloses an alloy that might be processed by the claimed method to form an oxidation

resistant surface. Therefore, for at least the reasons presented above for withdrawal of the § 103(a) rejections based on Szummer in view of Ono, the § 103(a) rejections of independent claims 1, 10 and 11 over Szummer in view of Linden also should be withdrawn.

Because independent claims 1, 10 and 11 would not have been obvious over Szummer in view of Linden, it follows that any claims that directly or indirectly depend from claims 1, 10 and 11 also would not have been obvious over the combination of Szummer and Linden. Therefore, Applicant requests withdrawal of the rejections based on Szummer and Linden as applied to claims 2-4 and 9, which ultimately depend from claim 1; and claims 13, 21 and 25-26, which ultimately depend from claim 11.

Claim Rejections 35 U.S.C. § 103(a) – Szummer in view of Uematsu

On page 12 of the Office Action, the Examiner rejects claims 1-5, 9-11, 13, 16, 18, 21 and 25-26 under 35 U.S.C. § 103(a) as having been obvious over Szummer in view of Japanese patent publication JP 06-172933 to Uematsu et al. ("Uematsu").

The Examiner alleges that Szummer discloses a method of preparing ferritic stainless steels as described in the rejection over Szummer in view of Ono, but concedes that Szummer does not specify that the ferritic stainless steels comprise at least 0.2 weight percent aluminum and a total weight of rare earth metals from 0.02 to 1.0 weight percent. The Examiner maintains Uematsu discloses adding 1 to 4.5 weight percent aluminum, to maintain high temperature oxidation resistance, and 0.01 to 0.15 weight percent rare earth metals such as cerium, lanthanum, and yttrium, to improve adhesion of the oxide film for a ferritic stainless steel having 15 to 25 weight percent chromium. The Examiner holds that it therefore it would have been obvious to one of ordinary skill in the art at the time the invention was made to have added 1 to 4.5 weight percent aluminum and 0.01 to 0.15 weight percent cerium, lanthanum, yttrium, and hafnium, as disclosed by Uematsu, to the ferritic stainless steel containing as disclosed by Szummer, in order to maintain high temperature oxidation resistance and improve adhesion of the film, as disclosed by Uematsu.

Applicant has established the deficiencies of Szummer as a primary reference in the above-discussed § 103(a) rejection of the claims of the Subject Application based on Szummer in view of Ono. For example, Szummer neither teaches nor suggests, and one having ordinary skill in the art would not have otherwise believed, that electropolishing a ferritic stainless steel would provide the features recited in claims 1, 10 and 11 of the Subject Application. No rational basis was provided for combining Szummer with Ono, and it was shown that an obviousness rejection could not be based on inherency when an inherent property was not known at the time the invention was made.

Applicant asserts the same arguments as bases for the withdrawal of the Examiner's § 103(a) rejections based on Szummer in view of Uematsu. As in the case of Ono, Uematsu merely discloses an alloy that might be processed by the claimed method to form an oxidation resistant surface. Therefore, for at least the reasons presented above for withdrawal of the § 103(a) rejections based on Szummer in view of Ono, the Examiner's § 103(a) rejections of independent claims 1, 10 and 11 over Szummer in view of Uematsu also should be withdrawn.

Because independent claims 1, 10 and 11 would not have been obvious over Szummer in view of Uematsu, it follows that any claims that directly or indirectly depend from claims 1, 10 and 11 also would not have been obvious over the combination of Szummer and Uematsu. Therefore, Applicant requests withdrawal of the rejections based on Szummer and Uematsu as applied to claims 2-4 and 9, which ultimately depend from claim 1; and claims 13, 16, 18, 21 and 25-26, which ultimately depend from claim 11.

Claim Rejections 35 U.S.C. § 103(a) – Szummer in view of Matsui

On page 16 of the Office Action, the Examiner rejects claims 1-5, 9-11, 13, 16, 18, 20-22 and 25-26 under 35 U.S.C. § 103(a) as having been obvious over Szummer in view of Japanese patent publication JP 09-209092 to Matsui et al. ("Matsui").

The Examiner alleges that Szummer discloses a method of preparing ferritic stainless steels (as described in the rejection over Szummer in view of Ono), but

concedes that Szummer does not specify that the ferritic stainless steels would comprise at least 0.2 weight percent aluminum and a total weight of rare earth metals from 0.02 to 1.0 weight percent. The Examiner maintains that Matsui discloses adding 0.1 to 2 weight percent aluminum, in order to improve high temperature oxidation (corrosion) resistance, and 0.001 to 0.05 weight percent rare earth metals such as yttrium, in order to improve the oxide film to stainless steel having 20 to 80 volume percent ferritic phase (ferritic stainless steel) and 15 to 27 weight percent chromium. The Examiner holds that, therefore, it would have been obvious to one of ordinary skill in the art at the time the invention was made to have added 0.01 to 2 weight percent aluminum and 0.001 to 0.05 weight percent rare earth metals, such as yttrium, as disclosed by Matsui, to the ferritic stainless steel disclosed by Szummer, in order to maintain high temperature oxidation resistance and improve adhesion of the oxide film, as disclosed by Matsui.

Applicant has established the deficiencies of Szummer as a primary reference in the above-discussed § 103(a) rejection of the claims of the Subject Application based on Szummer in view of Ono. For example, Szummer neither teaches nor suggests, and one having ordinary skill in the art would not have otherwise believed, that electropolishing a ferritic stainless steel would provide the features recited in claims 1, 10 and 11 of the Subject Application. No rational basis was provided for combining Szummer with Ono, and it was shown that an obviousness rejection could not be based on inherency when an inherent property was not known at the time the invention was made.

Applicant asserts the same arguments as bases for the withdrawal of the Examiner's § 103(a) rejections based on Szummer in view of Mitsui. As in the case of Ono, Mitsui merely discloses an alloy that might be processed by the claimed method to form an oxidation resistant surface. Therefore, for at least the reasons presented above for withdrawal of the § 103(a) rejections based on Szummer in view of Ono, the Examiner's § 103(a) rejections of independent claims 1, 10 and 11 over Szummer in view of Mitsui also should be withdrawn.

Because independent claims 1, 10 and 11 would not have been obvious over Szummer in view of Mitsui, it follows that any claims that directly or indirectly depend from claims 1, 10 and 11 also would not have been obvious over the combination of Szummer and Mitsui. Therefore, Applicant requests withdrawal of the rejections based on Szummer and Mitsui as applied to claims 2-4 and 9, which ultimately depend from claim 1; and claims 13, 16, 18, 20-22 and 25-26, which ultimately depend from claim 11.

Response to Declaration filed under 37 CFR § 1.132

Assuming only for the sake of argument that the Examiner has established a *prima facie* case of obviousness, Applicant maintains its earlier-presented position that any such a case is clearly rebutted by secondary considerations inasmuch as the corrosion resistance improvements obtained by the claimed method are wholly unexpected and significant. Applicant refers to the Declaration of Dr. Michael P. Brady ("the Brady Declaration"), a senior researcher at Oak Ridge National Laboratory, Oak Ridge, Tennessee, resubmitted in the previous response. As discussed in the Declaration, Dr. Brady has substantial experience in the area of oxidation of stainless steels and other alloys, has evaluated and developed ferritic stainless steels and related alloys for use in solid oxide fuel cells, and is experienced with electropolishing and other surface preparation techniques.

In his declaration, Dr. Brady attests that prior to the filing date of the Subject Application metallurgists did not believe that the high temperature oxidation resistance of ferritic stainless steels would be improved by electropolishing. The Examiner maintains that the Brady Declaration is unpersuasive because it fails to set forth evidence to substantiate the allegedly conclusory statements it sets forth. This basis for discounting the declaratory evidence is insufficient and cannot be maintained.

In paragraph 9 of the Brady Declaration, Dr. Brady declares:

At a time just prior to September 3, 2003, metallurgists conventionally believed that the high temperature oxidation resistance of a ferritic stainless steel surface would not be improved by electropolishing (flattening) the surface. Instead, metallurgists conventionally believed that mechanically deforming (roughening) the surface of a stainless steel would generally

improve oxidation resistance by allowing a greater concentration of chromium in the steel access to the surface, to form a protective scale on the surface. It was believed that because electropolishing flattened the steel's surface and thereby reduced surface roughness, access of chromium to the surface would be inhibited, and this would inhibit growth of the chromium-rich scale necessary to prevent oxidation. Confirmation of the conventional beliefs regarding surface roughness and oxidation resistance in alloys generally is provided in the following references: C. S. Giggins et al., "The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900°C and 1000°C", 245 Transactions of the Metallurgical Society of AIME at 2509-2514 (December 1969); and J. M. Rakowski et al., "The Effect of Surface Preparation on the Oxidation Behavior of Gamma TiAl-Base Intermetallic Alloys", 35 Scripta Materialia at 1417-1422 (1996). Both of these references suggest the advantage of a mechanically deformed surface in regards to oxidation resistance.

Accordingly, in addition to providing his own expert opinion on the subject, Dr. Brady references scientific journals in his declaration confirming that persons having ordinary skill in the metallurgical arts believed that roughening the surface of a stainless steel, and not flattening the surface, would improve oxidation resistance. Applicant also discussed this conventional belief in detail in a previous Office Action. Applicant respectfully refers the Examiner to that response for its discussion of what a person of ordinary skill in the art would have expected regarding surface roughness of stainless steels and oxidation resistance.

The present record is devoid of evidence wherein one had previously measured the oxidation resistance of electropolished ferritic stainless steels having the composition recited in the claims of the Subject Application or, for that matter, any other ferritic stainless steel. Thus, in order to predict the oxidation rate of electropolished stainless steels, a person of ordinary skill in the art at a time prior to the filing of the Subject Application would have relied on oxidation rate versus surface roughness information determined for mechanically roughened and mechanically polished stainless steels, as reported, for example, in the documents referenced in the Brady Declaration. Based on such reasoning, and with reference to the evidence in the references cited in the Brady Declaration, Dr. Brady was found the oxidation resistance results reported in

the Subject Application for electropolished ferritic stainless steel to be unexpected and surprising, as would any ordinarily skilled person in the metallurgical arts.

Applicant maintains that compelling evidence of unexpected results is included in the Subject Application and was confirmed by the Brady Declaration. Applicant further maintains that the statements presented by Dr. Brady in the Brady Declaration are not conclusory, but rather is uncontraverted expert testimony. The Examiner has identified no basis for discounting or rebutting Dr. Brady's statements, and Dr. Brady has submitted additional evidence with his declaration supporting his statements. Therefore, assuming only for the sake of argument that the Examiner has established a *prima facie* case of obviousness, the proffered evidence of surprising and unexpected rebuts any such determination. For that reason, the Examiner's § 103(a) rejections should be withdrawn and all claims should be allowed.

Conclusion:

Applicant asserts that the claims of the Subject Application are directed to subject matter that is patentable over the cited references. As such, Applicant respectfully requests that the Examiner issue a Notice of Allowance at an early date. If, however, the Examiner is of the opinion that the Subject Application is in condition for disposition other than allowance, Applicant respectfully requests that the Examiner contact Applicant's attorney at the telephone number listed below so that those concerns may be addressed.

Applicant's present response should not be taken as acquiescence to any of the specific rejections, assertions, statements, etc., presented in the Office Action that Applicant has not explicitly addressed herein. Applicant reserves the right to specifically address all such rejections, assertions, and statements in continuing applications, subsequent responses, and/or in appeal or pre-appeal proceedings.

Respectfully submitted,



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Metallographic Practices for Wrought Stainless Steels

METALLOGRAPHIC PROCEDURES used to prepare wrought stainless steels for macroscopic and microscopic examination are similar to those used for carbon and alloy steels and for tool steels (see the articles "Carbon and Alloy Steels" and "Tool Steels" in Volume 9, *Metallography and Microstructures*, of the *ASM Handbook*). However, certain types require careful attention to prevent artifacts. Because the austenitic grades work-harden readily, cutting and grinding must be carefully executed to minimize deformation. The high-hardness martensitic grades that contain substantial undissolved chromium carbide are difficult to polish while fully retaining the carbides. The most difficult of such grades to prepare is type 440C, particularly in the annealed or annealed and quenched condition. For the most part, preparation of stainless steels is reasonably simple if the basic rules for metallographic preparation are followed. However, unlike carbon, alloy, and tool steels, etching techniques are more difficult due to the high corrosion resistance of stainless steels and the vari-

ous second phases that may be encountered. References 1 to 3 provide additional details on the metallography of stainless steels.

Macroexamination

The procedures used to select and prepare stainless steel disks for macroetching are identical to those used for carbon, alloy, and tool steels. Because these grades are more difficult to etch, however, all surfaces to be etched must be smooth ground or polished. Saw-cut surfaces will yield little useful information if they are macroetched. The macroetching procedure is described in ASTM E 381 ("Standard Method of Macroetch Testing, Inspection, and Rating Steel Products, Comprising Bars, Billets, Blooms, and Forgings").

Macroetchants for stainless steels are listed in Table 1. Heated macroetchants are used with stainless steels in the same manner as carbon, alloy, or tool steels. Etchant compositions are often more complex and more aggressive. In the study of weld macrostructures, it is quite common to polish the section and use one of the general-purpose microetchants.

The standard sulfur print technique (Ref. 1) can be used to reveal the distribution of manganese sulfide (MnS) inclusions in stainless steels. However, if the manganese content of the grade is low, chromium will substitute for manganese in the sulfides, and the sulfur print intensity will decrease. As the manganese content decreases below approximately 0.60%, chromium substitutes for manganese. At manganese contents below approximately 0.20%, pure chromium sulfides will form. These produce no image in the sulfur print test.

Figure 1 shows the microstructure of a 480 mm (19 in.) diameter forged bloom of type 406 stainless steel that was made from a 1 m (40 in.) diameter ingot (Ref. 3). Due to its large size, the disk was quartered before macroetching with equal parts of hydrochloric acid (HCl) and water at 70 °C (160 °F). As might be expected, the grain structure is much finer at the surface than in the interior. Figure 2 shows the microstructure of a continuously cast 125 mm (5 in.) square billet of type 430 stainless steel in the as-cast condition. The disk was macroetched in the same manner as the forged type 406 bloom, but it was given a subsequent brightening/desmuting etch in a heated solution (also 70 °C, or 160 °F) of six parts water,

five parts nitric acid (HNO₃), and one part hydrofluoric acid (HF). The disk exhibits the classic pattern of very fine grains at the surface and columnar grains extending from this region to near the center, where the grains are equiaxed.

Microexamination

Sectioning techniques for stainless steels are identical to those used for carbon, alloy, or tool steels. Grades softer than approximately 35 HRC can be cut using a band saw or power hacksaw. However, such cutting produces substantial deformation and should be avoided with the deformation-sensitive austenitic grades. Deformation will be greatly reduced if cutting is performed using abrasive cutoff wheels with the proper degree of bonding. Shearing can be used with the ferritic grades but should be avoided with the austenitics. See the article "Sectioning" in Volume 9 of the *ASM Handbook* for additional information.

Mounting procedures, when required, are identical to those used for carbon, alloy, and tool steels. If edge preservation is required for near-surface examination, compression-mounting epoxy can be used, or specimens can be plated with electroless nickel. For specimens with surface cracks, it may be useful to vacuum impregnate the

Table 1 Macroetchants for stainless steels

Etchant	Comments
1. 50 mL HCl, 10 g CuSO ₄ (copper sulfate), 50 mL H ₂ O ₂	Marble's reagent. General-purpose macroetch; can be heated
2. 50 mL HCl, 50 mL H ₂ O, 30 mL 30% H ₂ O ₂	Mix HCl and H ₂ O, heat to 70-75 °C (160-170 °F). Immerse specimen and add H ₂ O ₂ in steps when foaming stops; do not mix.
3. (a) 15 g (NH ₄) ₂ S ₂ O ₈ (ammonium persulfate) and 75 mL H ₂ O (b) 250 g FeCl ₃ and 100 mL H ₂ O (c) 30 mL HNO ₃	Lehigh's No. 1 etch. Combine (a) and (b), then add (c); immerse specimen at room temperature; use fresh
4. 1 part HCl and 1 part H ₂ O	Standard hot etch. Use at 70-80 °C (160-180 °F), 15-45 min; desmut by dipping in warm 30% aqueous HNO ₃ solution to produce a bright surface
5. 10-40 mL HNO ₃ , 3-10 mL 48% HF, 25-50 mL H ₂ O	Use at 70-80 °C (160-180 °F); immerse until the desired degree of contrast is obtained
6. 50 mL HCl and 25 mL saturated CuSO ₄ in H ₂ O	Use at 75 °C (170 °F); immerse until the desired degree of contrast is obtained

(a) When water is specified, use distilled water.

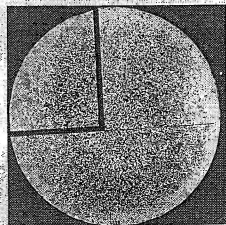


Fig. 1 Macrostructure of a 480 mm (19 in.) diam type 406 stainless steel forged bloom produced from a 1 m (40 in.) diam ingot. Courtesy of G.R. Vander Voort, Carpenter Technology Corp.

Table 2 Electropolishing procedures for stainless steels

Electrolyte composition	Comments
1. 50 mL HClO ₄ (perchloric acid), 750 mL ethanol, 140 mL H ₂ O(a)	Add HClO ₄ last, with care. Use at 8-20 V dc, 0.3-1.3 A/cm ² (1.9-8.4 A/in. ²), 20 °C (70 °F), 30-60 s. Rinse immediately after polishing.
2. 75 mL HClO ₄ , 90 mL H ₂ O, 730 mL ethanol, 100 mL butyl cellosolve	Add HClO ₄ last, with care. Use at 0.5-1.5 A/cm ² (3.2-9.7 A/in. ²), 20 °C (70 °F) max.
3. 62 mL HClO ₄ , 700 mL ethanol, 100 mL butyl cellosolve, 137 mL H ₂ O	Add HClO ₄ last, with care. Use at 1.2 A/cm ² (7.7 A/in. ²), 20 °C (70 °F), 20-25 s.
4. 25 g CrO ₃ , 133 mL acetic acid, 7 mL H ₂ O	Use at 20 V dc, 0.09-0.22 A/cm ² (0.38-1.4 A/in. ²), 17-19 °C (63-66 °F), 6 min. Dissolve CrO ₃ in solution heated to 60-70 °C (140-160 °F).
5. 37 mL H ₃ PO ₄ , 56 mL glycerol, 7 mL H ₂ O	Use at 0.78 A/cm ² (5.0 A/in. ²), 100-120 °C (212-250 °F), 5-10 min.
6. 6 mL HClO ₄ and 94 mL ethanol	Use at 35-40 V dc, 24 °C (75 °F), 15-60 s.

(a) When water is specified, use distilled water.

specimen in cold-setting epoxy; epoxy will be drawn into the cracks, minimizing bleedout problems after etching. See the article "Mounting of Specimens" in Volume 9 of the *ASM Handbook* for a complete discussion of mounting materials and problems associated with various mounting methods.

Grinding is performed using 120-, 240-, 320-, 400-, and then 600-grit water-cooled silicon carbide papers. Care must be taken, particularly when grinding austenitic grades, to remove the cold work from cutting and from each grinding step. In general, speeds of approximately 300 rpm and moderate, firm pressure are used. Grinding times are 1 to 2 min per step. If grinding is carried out by hand, the specimen should be rotated 45 to 90° between each step. Automatic grinding devices produce omnidirectional grinding patterns. See the article "Grinding, Abrasion, and Polishing" in Volume 9 of the *ASM Handbook* for additional information.

Polishing. After grinding, specimens are usually rough polished using 6- or 3-μm diamond as a paste, spray, or slurry on napless, low-nap, or medium-nap cloths. Edge flatness and inclusion retention are usually improved by using napless cloths, although scratch removal may not be as complete as with medium-nap cloths. A lubricant extender compatible with the diamond abrasive should be used to moisten the cloth and reduce drag. A wheel speed of approximately 150 rpm is usually adequate. Pressure should be moderate and firm; specimen rocking should be avoided if polishing is carried out by hand.

For hand polishing, rotate the specimen around the wheel in the direction opposite to wheel rotation while moving from center to edge. Automatic devices generally produce better edge flatness than hand polishing. After this step, the

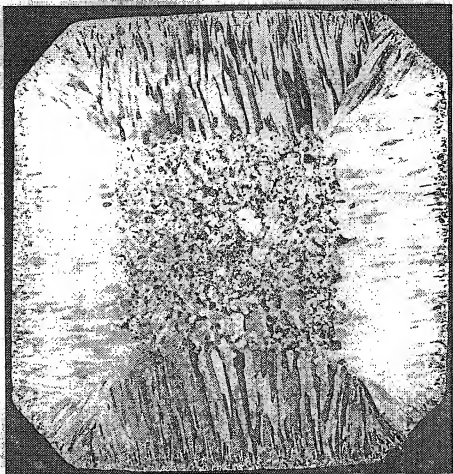


Fig. 2 As-cast microstructure of a 125 mm (5 in.) square billet of continuously cast type 430 stainless steel. Courtesy of G.J. Vander Voort, Carpenter Technology Corp.

specimen may be polished using 1 μm diamond abrasive on a medium-nap cloth. For routine examination, a 1 μm diamond finish may be adequate, particularly for the hardenable grades.

To produce high-quality, scratch-free surfaces suitable for photomicroscopy, specimens should be final polished using one or more fine abrasives. The most commonly used final abrasives are 0.3 μm α-alumina (Al₂O₃) or 0.05 μm γ-Al₂O₃. Medium-nap cloths are usually used. Polishing with these abrasives, using a polish mixed as a water slurry, is performed in the same manner as diamond polishing. Specimens should be carefully cleaned between each rough and final polishing step to avoid contamination at the next step. Colloidal silica is a highly suitable final abrasive for stainless steels.

Stainless steels, particularly the austenitic grades, are often polished electrolytically. In most cases, electropolishing is performed after grinding to a 600-grit silicon carbide finish. Table 2 lists recommended procedures. Electropolishing usually produces high-quality, deformation-free surfaces; however, inclusion attack is encountered, and second phases may be attacked preferentially.

Etching. For inclusion examination, etching is not required, although it is necessary for examining the microstructure. Although stainless steels are reasonably easy to polish, etching is generally a more difficult step. The corrosion resistance of stainless steels and the potential microstructural complexity of these alloys make selection of the best etchant a more difficult problem than for carbon and alloy steels.

Stainless steel etchant ingredients are dissolved in water, methanol, or ethanol; glycerol; or a mixture of these solvents. Reagents with alcohol or glycerol as the solvent provide better wetting of the surface than water-based reagents and generally provide more uniform etching. Because alcohol reduces dislocation, alcohol-based reagents can be made more concentrated without becoming too powerful for controlled etching. Stainless steel surfaces passivate; therefore, reducing conditions are preferred to oxidizing conditions that promote passivity. Consequently, stainless steel etchants often contain HCl, sulfuric acid (H₂SO₄), or HF acid, although HNO₃ may be used alone or mixed with HCl to produce aqua regia or a modified aqua regia. Swabbing, instead of immersion, may be desired to obtain more

uniform etch results. Electrolytic etching is also very popular, because it produces uniform etching, is easier to control, and gives reproducible results. Numerous etchants have been proposed for stainless steels; each has advantages and disadvantages.

Etching the 400-series ferritic or martensitic grades is simpler than the 200- or 300-series austenitics or the 600-series precipitation-hardenable grades. Vilella's reagent (4% picric + HCl) or superalloy is commonly used with ferritic and martensitic grades. Etching of the extra-low-interstitial-content ferritic grades to observe the grain boundaries, however, is much more difficult than with the ordinary ferrites. Microetchants are listed in Table 3.

Etching of the austenitic grades to examine the grain structure is difficult with most standard reagents. As shown in the photomicrographs in the article "Microstructures of Wrought Stainless Steels" in this Volume, most of the standard reagents reveal only some of the grain boundaries. Tint etching, which requires a high-quality polish for good results, reveals all of the grains by color contrast. To measure the grain size when a more accurate value is required than can be obtained by a comparison chart rating, all the boundaries must be revealed. Twin boundaries are ignored.

Sensitizing the specimen by heating it for 1 to 6 h at 650 °C (1200 °F) will facilitate observation of the grain boundaries. An alternate technique (Ref. 4, 5) involves electrolytically etching the solution-annealed specimen in 50% aqueous HNO₃ (see Table 3). With this procedure, twin boundaries are not revealed. This etch will also bring out prior-austenite grain boundaries in solution-annealed, but not aged, precipitation-hardened grades. For structure-property correlations, the mean lineal intercept value for grain and twin boundaries should be measured, because the twin boundaries also contribute to strengthening. Such a measurement should not be converted to a grain size value.

Various alkaline ferricyanide reagents, such as Murakami's reagent, have been widely used to etch austenitic stainless steels for phase identification. The colors produced by these etchants vary with etchant composition, temperature, time, and phase orientation. When using a particular reagent in the prescribed manner, the colors obtained may differ from those reported in the literature. However, the etch response, that is, what is attacked and what is not attacked, is highly reproducible.

When using the standard formulation of Murakami's reagent at room temperature, for example, the carbides will be attacked in 7 to 15 s; α -phase will be only lightly attacked after 3 min. If higher concentrations of potassium hydroxide (KOH) or sodium hydroxide (NaOH) and potassium ferricyanide (K₃Fe(CN)₆) are used at room temperature, α -phase will be attacked instead of the carbides. Using boiling, the standard formulation attacks ferrite, carbide, and δ -phase, although some evidence indicates that δ -phase will not be attacked. Therefore, when using this reagent or one of its numerous modifications, directions should be followed carefully. Ex-

Table 3 Microetchants for stainless steel

Etchant	Comments	Etchant	Comments
1. 1 g picric acid, 5 mL HCl, 100 mL ethanol	Vilella's reagent. Use at room temperature to 1 min. Outlines second-phase particles (carbides, δ phase, δ -ferrite), etches martensite.	14. 10 g NaCN (sodium cyanide) and 100 mL H ₂ O	Electrolytic etch at 6 V dc, 25-mm spacing, 5 min, platinum cathode. Sigma darkened, carbides light. Ferrite-quenched, austenite not attacked. Good for revealing carbides. Use with care under a hood.
2. 1.5 g CuCl ₂ (cupric chloride), 33 mL HCl, 33 mL ethanol, 33 mL H ₂ O(a)	Kalling's No. 1 reagent for martensitic stainless steels. Use at room temperature. Martensite dark, ferrite colored, austenite not attacked.	15. 10 mL HCl and 90 mL methanol	Electrolytic etch at 1.5 V dc, 20 °C (70 °F) to attack δ phase. Use at 6 V dc for 3-5 s to reveal structure.
3. 5 g CuCl ₂ , 100 mL HCl, 100 mL ethanol	Kalling's No. 2 reagent. Use at room temperature. Ferrite attacked rapidly, austenite slightly attacked, carbides not attacked.	16. 60 mL HNO ₃ and 40 mL H ₂ O	Electrolytic etch to reveal austenite grain boundaries (but not twins) in austenitic grades. With stainless steel cathode, use at 1.1 V dc, 0.075-0.14 A/cm ² (0.48-0.90 A/in. ²), 120 s. With platinum cathode, use at 0.4 V dc, 0.015-0.066 A/cm ² (0.35-0.45 A/in. ²), 45 s. Will reveal prior-austenite grain boundaries in solution-treated (but not aged) martensitic precipitation-hardenable alloys.
4. 5 g CuCl ₂ , 40 mL HCl, 30 mL H ₂ O, 25 mL ethanol	Fry's reagent. For martensitic and precipitation-hardenable grades. Use at room temperature.	17. 50 g NaOH and 100 mL H ₂ O	Electrolytic etch at 2-4 V dc, 5-10 s to reveal α phase in austenitic grades.
5. 4 g CuSO ₄ , 20 mL HCl, 200 mL H ₂ O	Marble's reagent. Used primarily with austenitic grades. Use at room temperature to 10 s. Attacks α phase.	18. 56 g KOH and 100 mL H ₂ O	Electrolytic etch at 1.5-3 V dc for 3 s to reveal α phase (red-brown) and ferrite (dark brown). Oil colored same as sigma.
6. 3 parts glycerol, 2-5 parts HCl, 1 part HNO ₃	Glyceric. Popular etch for all stainless grades. Higher HCl content reduces pitting tendency. Use fresh, never store. Discard when reagent is orange colored. Use with care under a hood. Add HNO ₃ last. Immerse or swab a few seconds to 4 minutes. Attacks α phase, outlines carbides. Substitution of water for glycerol increases attack rate.	19. 20 g NaOH and 100 mL H ₂ O	Electrolytic etch at 20 V dc, for 5-20 s to outline and color δ -ferrite tan.
7. 45 mL HCl, 15 mL HNO ₃ , 20 mL methanol	Methanolic aqua regia. Used with austenitic grades to reveal grain structure; outline ferrite and α phase.	20. NH ₄ OH (some)	Electrolytic etch at 1.5-4 V dc for 10-60 s. Very selective. At 1.4 V dc, carbide completely etched in 40 s. Sigma unaffected after 180 s. At 6 V dc, α phase etched after 40 s.
8. 15 mL HCl, 5 mL HNO ₃ , 100 mL H ₂ O	Dilute aqua regia for austenitic grades. Uniform etching of austenite, outlines carbides, α phase, and ferrite (sometimes attacked).	21. 10 g (NH ₄) ₂ SiF ₆ and 100 mL H ₂ O	Use at 6 V dc for 10 s to color carbide dark brown.
9. 4 g KMnO ₄ (potassium permanganate), 4 g NaOH, 1 mL H ₂ O	Groesbeck's reagent. Use at 60-90 °C (140-195 °F) to 6 min. Colors: carbides dark, α phase gray, ferrite and austenite not affected.	22. 200 mL HCl and 1000 mL H ₂ O	Beraha's tint etch for austenitic, duplex, and precipitation-hardenable grades. Add 0.5-1.0 g K ₂ S ₂ O ₈ per 100 mL of solution (if heating is too rapid, use a 10% aqueous HCl solution). Immerse at room temperature (never swab) for 30-120 s until surface is reddish.
10. 30 g KMnO ₄ , 30 g NaOH, 100 mL H ₂ O	Modified Groesbeck's reagent. Use at 90-100 °C (195-212 °F) for 20 s to 10 min to color ferrite dark in duplex alloys. Austenite not affected.		Austenitic colored, carbides not colored. Longer immersion colors ferrite lightly. If coloration is inadequate, add 2 g NH ₄ F (ammonium bifluoride) to stop reaction at left.
11. 10 g K ₃ Fe(CN) ₆ , 10 g KOH or 7 g NaOH, 100 mL H ₂ O	Murakami's reagent. Use at room temperature to 60 s to reveal carbides; α phase faintly revealed by etching to 3 min. Use at 80 °C (176 °F) to boiling to 60 min to darken carbides. Sigma may be colored blue, ferrite yellow to yellow-brown, austenite not attacked. Use under a hood.	23. 20 g picric acid and 100 mL HCl	Etch by immersion. Develops grain boundaries in austenitic and δ -ferrite in duplex alloys.
12. 30 g KOH, 30 g K ₃ Fe(CN) ₆ , 100 mL H ₂ O	Modified Murakami's reagent. Use at 55 °C (130 °F) for 5 s. Colors of phase reddish brown, ferrite dark gray, austenite unattacked, carbide black. Use under a hood.	24. Saturated aqueous Ba(OH) ₂ (barium hydroxide)	Attacks carbides well before α phase in austenitic grades when etched at 1.5 V dc, but attacks both equally when used at 3-6 V dc. Has been used to differentiate α phase and Laves phase (use at 4.5 V dc, platinum cathode, 20 s). Chi is stained mottled-purple. Laves is not colored; ferrite is stained tan.
13. 10 g ascorbic acid and 100 mL H ₂ O	Popular electrolytic etch, 6 V dc, 25-min spacing, 15-30 s reveals carbides, grain boundaries revealed after 45-60 s. α phase outlined after 6 s. Lower voltages (1-3 V dc) can be used. Dissolves carbides. Sigma strongly attacked, austenite moderately attacked, ferrite not attacked.	25. 50 mL each H ₂ O, ethanol, methanol, and HCl; plus 1 g CuCl ₂ , 3.5 g FeCl ₃ , 2.5 mL HNO ₃	Can be stirred. General-purpose etch for most stainless steels. Does not attack grades in free-machining families.

(a) When water is specified, use distilled water.

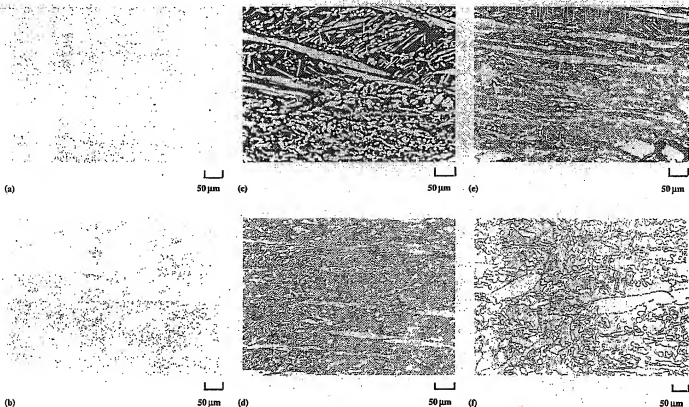


Fig. 3 A comparison of various etchants to reveal the microstructure of 7-Mo PLUS duplex stainless steel (longitudinal plane). (a) Glyceregia chemical etch. (b) Eriaholic 15% HCl chemical etch. (c) Berah's tint etch to color the ferrite. (d) Electrolytic 20% NaOH to color the ferrite. (e) Electrolytic 56% KOH to color the ferrite. (f) Electrolytic 60% HNO₃. All at 200x. Courtesy of G.J. Vander Voort, Carpenter Technology Corp.

perimentation with specimens of known constitution is also recommended.

Electrolytic reagents, which are used often with austenitic and duplex grades, provide greater control of the etching process and are highly reproducible. Perhaps the most commonly used electrolytic reagent is 10% aqueous oxalic acid, which will reveal carbides after a short etch if they are present (see Table 3). When carbides are not present, the austenite grain boundaries will be revealed in 15 to 60 s. If ferrite is present, it will be outlined after 10 to 15 s.

Electrolytic reagents are generally quite simple in composition. The selectivity of electrolytic reagents based on various hydroxide solutions has been demonstrated (Ref 6). Strong hydroxide solutions attack α -phase preferentially to carbides; weak hydroxide solutions attack carbides much more readily than α -phase. Therefore, to reveal α -phase, 10 N KOH is employed, and to reveal carbides, concentrated ammonium hydroxide (NH₄OH) is used. For intermediate-strength hydroxide solutions, etching response is altered by a change in the applied potential.

Several sequential etching procedures have been suggested for phase identification in austenitic stainless steels. One procedure (Ref 6) involves etching first with Vilella's reagent to

outline the phases present. Next, the specimen is electrolytically etched with 10 N KOH at 3 V dc for 0.4 s to color α -phase, if present, but not carbides. The specimen is then electrolytically etched with concentrated NH₄OH at 6 V dc for 30 s to color any carbides present. Another procedure (Ref 7) also begins with Vilella's reagent to reveal the constituents. Next, Murakami's reagent is used at room temperature to stain the carbides present. Any α -phase or δ -ferrite present is unaffected. Finally, the specimen is electrolytically etched with aqueous chromium trioxide (CrO₃), which will attack carbides and α -phase, but not δ -ferrite. Murakami's reagent does not attack carbides in titanium- or niobium-stabilized stainless steels. These carbides are attacked slowly in electrolytic CrO₃.

Delta-ferrite in martensitic, austenitic, or precipitation-hardenable grades can be preferentially colored by electrolytic etching with 20% aqueous NaOH at 20 V dc for 5 to 20 s. This procedure outlines and uniformly colors tan δ -ferrite. Although the color varies with orientation, 10 N KOH also colors δ -ferrite.

Potentiostatic etching (Ref 1 and 8) is frequently used for selective etching of constituents in stainless steels. This technique is similar to electrolytic etching, except a third electrode is in-

cluded to monitor the etch potential, which is controlled using a potentiostat. This technique affords the greatest possible control over etching.

Heat tinting is a useful technique with austenitic stainless steels. Phase delineation is improved by first etching with a general-purpose reagent, such as Vilella's. The specimen is then heated in air at 500 to 700 °C (930 to 1290 °F); 650 °C (1200 °F) has been most commonly used with times to 20 min. Austenite is colored more readily than ferrite, and carbides resist coloration longest. After 20 min at 650 °C (1200 °F), austenite is blue-green, α -phase is orange, ferrite is light cream, and carbides are uncolored.

Magnetic colloids have also been used to detect ferromagnetic constituents in austenitic stainless steels. This technique, which is referred to as *magnetic etching*, has been extensively applied using a ferromagnetic colloid solution (Ferrolflux) containing very fine magnetic particles (Ref 9). Delta-ferrite and strain-induced martensite are readily identified by this method. More detailed information on magnetic etching can be found in Volume 9 of the *ASM Handbook* (see Appendix 1 to the article "Etching").

Figure 3 illustrates the use of a variety of etchants to reveal the structure of a duplex stainless steel (UNS S32950, also known as Carpenter

Table 4. Electropolishing procedures for preparing thin-foil stainless steel specimens

Solution composition	Comments
1. 5 or 10 mL HClO ₄ and 95 or 90 mL acetic acid at 20 V dc	Popular electropolishing for stainless steels. Used for window technique or for perforation of disk specimens. Keep solution cool.
2. (a) 10 mL HNO ₃ and 90 mL H ₂ SO ₄ at 30 V dc (b) 10 mL HClO ₄ , 20 mL glycerol, 70 mL ethanol at 65 V dc	Popular procedures for austenitic grades. Use (a) for electropolishing specimens, then (b) for perforation.
3. 10 mL HClO ₄ and 90 mL ethanol at 12 V dc, 0 °C (32 °F)	Popular electropolishing for stainless steels. Use for perforation.
4. 40 mL H ₂ SO ₄ and 60 mL H ₃ PO ₄ at 35 V dc; 0.3 A/cm ² (1.9 A/in. ²)	Electropolishing for stainless steels for perforation.
5. 25 g NaOH, 133 mL acetic acid, 7 mL H ₂ O at 20 °C (70 °F)	Electropolishing for stainless steels. Good for window method. Opacity of solution makes it difficult to use for jet perforation.
6. (a) 40 mL acetic acid, 30 mL H ₂ SO ₄ , 20 mL HNO ₃ , 10 mL H ₂ O at 80-120 V dc, 0.1 A/cm ² (0.65 A/in. ²) (b) 54 mL H ₂ PO ₄ , 36 mL H ₂ SO ₄ , 10 mL ethanol at 6 V dc	Procedure for martensitic grades. Jet electropolishing disks with (a) prior to final thinning with (b) to perforation.
7. 45 mL H ₂ SO ₄ , 30 mL H ₂ SO ₄ , 25 mL H ₂ O at 6 V dc	Procedure for austenitic grades for perforation

(a) When water is specified, use distilled water.

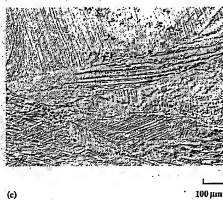
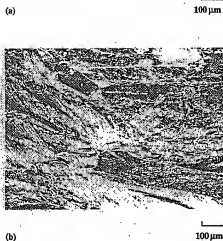


Fig. 4 A comparison of various light microscope illumination modes to reveal the microstructure of a warm-worked high-manganese drill collar alloy (as-polished) etched in acetic glycerol and viewed with (a) bright-field illumination, (b) dark-field illumination, and (c) differential interference contrast illumination. All three photomicrographs show the same area. Courtesy of G.F. Vander Voort, Carpenter Technology Corp.

7-Mo PLUS. Table 3 should be consulted for procedure details.

Illumination modes other than bright field are of considerable value for examining stainless

steels (Ref 3). Oblique illumination or differential interference contrast (DIC) can be used to observe second-phase constituents more clearly, in the as-polished condition if there is a hardness difference, or after etching. The DIC illumination mode is also useful for examining grain structure, as is dark-field illumination. Polarized light was very limited use with stainless steels.

As an example of the use of various illumination modes, Fig. 4 demonstrates the superiority of dark-field illumination and DIC in revealing the structure of a high-manganese warm-worked drill collar austenitic stainless steel in the as-rolled condition. This figure shows that the bright field micrograph (Fig. 4a) is nearly featureless; however, the use of the dark-field mode (Fig. 4b) or DIC (Fig. 4c) reveals the deformed substructure clearly. Additional information on illumination modes associated with the light microscope can be found in the article "Optical Microscopy" in Volume 9 of the *ASM Handbook*.

Electron Microscopy. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to examine the fine structure of stainless steels and for phase identification. Scanning electron microscopy examination uses the same specimens as optical (light) microscopy. As-polished specimens often can be examined, although etching is more common. Many second-phase constituents can be observed using backscattered elec-

tron detectors due to the adequate atomic number contrast between these phases and the matrix. However, secondary electron images produced from topographic contrast and atomic number contrast are most often used. Energy-dispersive x-ray analysis (EDXA) is prevalent for chemical analysis of second phases, although lightweight elements, such as carbon and nitrogen, cannot be detected unless thin-window or windowless EDXA detectors or wavelength-dispersive detectors are used. Detailed reviews of SEM, TEM, and EDXA can be found in Volumes 9, 10, and 12 of the *ASM Handbook*.

Transmission electron microscopy requires preparation of replicas or thin-foil specimens (see the article "Transmission Electron Microscopy" in Volume 9 of the *ASM Handbook*). Replicas may be made to reveal the outline and topography of the phases, or if the specimen is deeply etched, second-phase particles may be extracted. Extraction replicas permit analysis of second phases by electron diffraction and by EDXA. Thin-foil specimens can also be analyzed by these methods, although interference from the matrix is possible. Table 4 lists electropolishing procedures for producing stainless steel thin foils. Reference 10 is another excellent source of information on thin foil specimen preparation techniques for TEM examination.

Bulk Extractions. Although bulk samples can be directly analyzed by x-ray diffraction for phase identification, it is quite common to extract the second phases chemically and analyze the extracted particles. This eliminates the matrix and concentrates the second phase, facilitating identification of small amounts of the second-phase constituents. Bulk extraction of phases from wrought stainless steels is performed using electrolytes such as 10% HCl in methanol. Details concerning the use of such electrolytes are given in Ref 11 to 13.

ACKNOWLEDGMENT

The information in this article is largely taken from G.F. Vander Voort and H.M. James, *Wrought Stainless Steels, Metallography and Microstructures*, Vol 9, *ASM Handbook* (formerly 9th ed. *Metals Handbook*), ASM International, 1985, p 279-296.

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ASM Specialty Handbook[®]

Stainless Steels

Edited by
J.R. Davis
Davis & Associates

Prepared under the direction of the
ASM International Handbook Committee

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First printing, December 1994

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Library of Congress Cataloging-in-Publication Data

Stainless Steels / edited by J.R. Davis;

Prepared under the direction of the ASM International Handbook Committee
p. cm.—(ASM Specialty Handbook)

1. Steel, Stainless

I. Davis, J.R. (Joseph R.)

II. ASM International. Handbook Committee.

III. Series

TA479.S7S677 1994 620.1'7—dc20

SAN: 204-7586

ISBN: 0-87170-503-6

ASM International®
Materials Park, OH 440730002

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